Purification of olefin-containing feed streams in polymerization or alkylation processes

The present invention relates to a process for purifying olefin-containing feed streams in polymerization or alkylation processes and also to processes for preparing alkylbenzenes by catalytic reaction of benzene and olefins.

Ethylbenzene is predominantly obtained by catalytic alkylation of benzene using ethylene. Aluminum chloride is used as catalyst in the liquid phase while Lewis acids or synthetic zeolites are used as catalysts in the gas phase. Zeolites are highly active catalysts both for alkylation and for transalkylation. Although the zeolite catalysts are less susceptible to water, sulfur and other catalyst poisons, they lose their activity as time goes on and have to be regenerated periodically.

Various methods of prolonging the life of zeolite catalysts for alkylation reactions have been proposed. WO 98/07673 describes the alkylation of benzene using, for example, propylene. The benzene was pretreated by passing it over mordenites.

According to WO 89/12613, the life of zeolite catalysts in the transalkylation of polyalkylbenzenes can be increased by addition of gaseous hydrogen.

US 5,030,786 proposes reducing the water content of the aromatic feed stream to below 100 ppm in the alkylation or transalkylation reaction over zeolite catalysts. On the other hand, WO 93/00992 finds that, particularly in the running-up phase, the zeolite catalyst in the alkylation or transalkylation should have a minimum water content of more than 3.5% by weight, based on the catalyst composition.

Most ethylene is produced in steam crackers. The ethylene content is generally above 99.9% by weight. In addition, it contains small amounts of sulfur, oxygen, acetylene, hydrogen, carbon monoxide and carbon dioxide. Apart from the production of ethylbenzene, ethylene is used in large amounts for polymerization to form polyethylenes such as HDPE, LDPE and LLDPE. Polymerization in particular is carried out using a "polymer grade ethylene".

It is an object of the present invention to find a process for improving the activity of catalysts for olefin polymerization. Furthermore, a process for prolonging the life and reducing the

recycling times of alkylation or transalkylation catalysts in the catalytic alkylation of benzene using olefins, particularly over zeolite catalysts, is to be found.

We have found that this object is achieved by a process for purifying olefin-containing feed streams in polymerization or alkylation processes, which comprises passing the feed stream over an adsorption layer.

In principle, the process can also be used for olefin-containing feed streams in other processes. However, it is particularly suitable for polymerization and alkylation processes in which catalysts which are sensitive to very small amounts of impurities are used.

Preferred embodiments may be found in the subordinate claims 2 to 10.

Adsorbents suitable for the adsorption layer are carbon-containing adsorbents such as carbon blacks, activated carbon or carbon molecular sieves, oxygen-containing compounds such as aluminum oxides, silica gels, natural or synthetic aluminates, silicates, aluminum silicates or zeolites and molecular sieves. Structure, properties and preparation of zeolites are described, for example, in Zeolite Molecular Sieves, Donald W. Breck, John Wiley&Sons, 1974; Atlas of Zeolite Structure Types, 3rd Ed. W.M. Meier and D. H. Olson, Butterworth-Heinemann, 1992 or Handbook of Molecular Sieves, R. Szostak, Chapman&Hall, New York, 1992. Preferred zeolites are those of the types ZSM-5, ZSM-11, ZSM-12, ZSM-22, ZSM-23, ZSM-35, ZSM-48, beta-zeolite, zeolite Y, dealuminated zeolite Y, mordenites, zeolite MCM-22, MCM-41, MCM-49 and MCM-56. Preference is also given to alumina or activated aluminum oxide, particularly for alkaline impurities. Fuller's earths are also sometimes used. Owing to the surface properties, preference is given to using carbon-containing adsorbents for organic and nonpolar impurities.

In general, the adsorbents are used in the form of spheres, rods or granules having an external dimension of from 1 to 10 mm.

The process of the present invention can be carried out in adsorbers containing fixed, moving or fluidized beds, batchwise or continuously. The adsorption layer is particularly preferably located in a fixed-bed reactor. Use is advantageously made of two or more fixed-bed adsorbers which can be operated alternately for the purification of the olefin stream and for regeneration. The

size of the adsorber depends on the type and amount of impurities and on the desired regeneration cycles.

In general, the olefin feed stream is passed over the adsorption layer at from 0 to 300°C, preferably from 50 to 250°C, and a pressure in the range from 1 to 45 bar.

As olefin, preference is given to using ethylene or propylene. Particular preference is given to using "polymer grade" ethylene. Typical specifications for ethylene may be found in Ullmann, Encyl. of Industrial Chemistry, Vol. A10, page 87, and Kirk-Othmer, Encyclopedia of Chemical Technology, 4th Edition, Vol 9, page 907.

The process of the present invention is preferably used for the pretreatment of ethylene or propylene feed streams in the catalytic alkylation of benzenes, in particular by means of alkylation reactions catalyzed by Lewis acids or zeolites. Such processes are described, for example, in Ullmann, Encycl. of Industrial Chemistry, 5th Ed. Vol A10, pages 35 to 43. It is particularly preferably used in the zeolite-catalyzed alkylation or transalkylation of benzene and ethylene. Such processes and suitable catalysts are described, for example, in US 5,902,917, US 4,891,448, US 5,081,323, US 5,198,595, US 5,243,116 or WO 98/07673.

In the zeolite-catalyzed alkylations, the adsorption layer particularly preferably comprises a zeolite of the same type as the zeolites used for the catalyst or a zeolite having similar pore diameters and pore size distribution.

In the alkylation of benzene, not only the ethylene or propylene feed stream but also the feed streams comprising benzene or alkylbenzene and polyalkylbenzene are advantageously passed over an appropriate adsorption layer. Adsorbents which can be used for this purpose are those which are used for the olefin feed stream.

Examples

Example 1

330 kg of predried ethylene containing 6 ppb (10^{-9} kg/kg) of organically bound nitrogen (total organic nitrogen = TON) from the steam cracker of BASF Aktiengesellschaft in Ludwigshafen were passed through a 5 000 mm long column having a diameter of 50 mm for 1 week at room temperature. The column was packed with 330 g of Selexsorb COS® (fill height 2 000 mm). The ethylene flow was

26 liters/min. The adsorbent was then flushed with nitrogen having a temperature of 300°C (20 liters/h) for 5 hours. During this treatment, the adsorbed, basic, nitrogen-containing compounds were desorbed from the Selexsorb COS. The nitrogen was passed through wash bottles in which 0.1N H_2SO_4 was present. The basic compounds were converted into their sulfuric acid salts in this way. The content of N-containing basic compounds in the washing liquid was determined by the chemiluminescence method (ASTM D 6069).

Examples 2 to 4

Example 1 was repeated using the adsorbents indicated in the table. In Examples 3 and 4, desorption was achieved by elution of the adsorbent with 1N H_2SO_4. The results are shown in the table. The recovery is a measure of the adsorption efficiency.

Table: Purification of ethylene containing 6 ppb of TON (total organic nitrogen)

Example	Adsorbent	Desorption	Adsorbed amount of TON** in 10^{-9} kg of N/kg of ethylene	Recovery in %
1	Selexsorb COS	Nitrogen, 300°C	4	67
2	Sylobead MS 544 HP	Nitrogen, 300°C	2	33
3	Amberlyst 36 W	1N H_2SO_4	5	83
4	Tonsil CO 614 G	1N H_2SO_4	5	83

Adsorbents:

A: Selexsorb COS: activated aluminum oxide from Alcoa

B: Sylobead MS 544 HP: highly porous, crystalline aluminum silicate from Grace Davison, pore diameter about 10 Å

C: Amberlyst 36 W: sulfonated divinylbenzene-styrene copolymer from Rohm & Haas

D: Tonsil CO 614 G: aluminum silicate from Süd-Chemie